

Att rn y D ck t No. 05725.0407-01 Application N :: 09/832,877

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In Re Application of:

Roland DE LA METTRIE et al.

) G

Group Art Unit: 1751

Examiner: Not yet assigned

Application No.: 09/832,877

Filed: April 12, 2001

For: OXIDIZING COMPOSITION COMPRISING AND USES FOR DYEING,

FOR PERMANENTLY RESHAPING OR FOR BLEACHING KERATIN

**FIBRES** 

Assistant Commissioner for Patents

Washington, D.C. 20231

Sir:

RECEIVED
TC 1700

## REQUEST FOR CORRECTED PATENT APPLICATION PUBLICATION UNDER 37 C.F.R. § 1.221(b)

On December 13, 2001, the Office published the above-identified application No. 09/832,877 as Publication No. US-2001/0049849-A1. The published application contains material mistakes that are the fault of the Office. Attached hereto is a copy of each relevant page of the originally filed application and a marked-up copy of the corresponding page of the published application containing the mistakes.

A mistake is material when it affects the public's ability to appreciate the technical disclosure of the patent application publication or determine the scope of the provisional rights that an applicant may seek to enforce upon issuance of a patent. See C.F.R. § 1.221(b).

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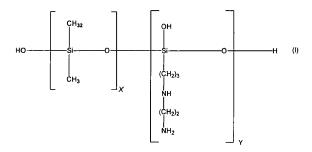
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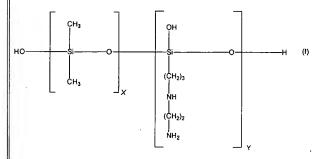
## Attorney Docket No. 05725.0407-01 - Application No.: 09/832,877

The mistakes, which are indicated in red ink on the relevant pages of the marked-up copy of the published application attached hereto, are as follows:

1. In paragraph 32, the published application recites as formula (I)



However, the originally filed application recites as formula (I):



The error is that the published application recites "CH<sub>32</sub>" rather than "CH<sub>3</sub>." This mistake, therefore, results in the disclosure of an erroneous formula. Thus, this mistake is material as it may affect the public's ability to appreciate the technical disclosure of the patent application publication. For at least this reason, this mistake is material and accordingly should be corrected.

2. In paragraphs 43 through 46, the groups disclosed are wrong.

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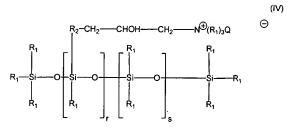
Specifically, the published application recites:

$$-N \xrightarrow{\bigoplus} (R')3A^-,$$
 $-N \xrightarrow{\bigoplus} (R')2(H)A^-,$ 
 $-N \xrightarrow{\bigoplus} (R')(H)2A^-,$ 
 $-N(R)-CH_2-CH_2-N^{61}(R')(H)2A^-.$ 

whereas, it should recite:

These mistakes are material as they may affect the public's ability to appreciate the technical disclosure of the patent application publication. For at least this reason, these mistakes are material and accordingly should be corrected.

3. In paragraph 50 of the published application, the formula (IV) recites:



whereas, it should recite:

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 $R_{1} = \begin{bmatrix} R_{2} - CH_{2} & CHOH - CH_{2} & N^{\bigoplus}(R_{1})_{3}Q^{\bigoplus} \\ R_{1} - Si & O & Si & O & Si & R_{1} \\ R_{1} & R_{1} & R_{1} & R_{1} \end{bmatrix}_{f}$ 

The error is that the sign " is not beside the Q group, and thus does not accurately represent that the Q group is a negatively charged ion, and may be erroneously interpreted as representing that the entire cationic silicone polymer of formula (IV) is negatively charged. This mistake is material as it may affect the public's ability to appreciate the technical disclosure of the patent application publication. For at least this reason, this mistake is material and accordingly should be corrected.

4. In lines 5-6 of paragraph 63, the published application recites "a nonionic surfactant of formula:  $C_8H_{27}$ - $C_6H_4$ - $(OCH_2CH_2)_{40}$ -OH." However, this should recite "a nonionic surfactant of formula:  $C_8H_{17}$ - $C_6H_4$ - $(OCH_2CH_2)_{40}$ -OH." The error is that the group " $C_8H_{27}$ " should be " $C_8H_{17}$ ." This mistake, therefore, results in the disclosure of an erroneous formula. Thus, this mistake is material as it may affect the public's ability to appreciate the technical disclosure of the patent application publication. For at least this reason, this mistake is material and accordingly should be corrected.

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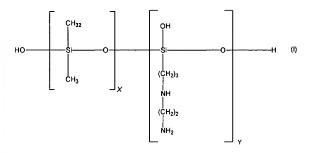
- 5. In line 3 of paragraph 81, the published application recites "with a C<sub>1</sub>-C<sub>4</sub>, alkyl radical," whereas this should recite "with a C<sub>1</sub>-C<sub>4</sub> alkyl radical." . The error is that there is a comma between "C<sub>4</sub>" and "alkyl." This mistake may be erroneously interpreted as reciting other than C<sub>1</sub>-C<sub>4</sub> alkyl radical. Thus, this mistake is material as it may affect the public's ability to appreciate the technical disclosure of the patent application publication. For at least this reason, this mistake is material and accordingly should be corrected.
- 6. In lines 3-4 of paragraph 87, the published application recites "N,N'-bis(ß-hydroxyethyl)-N, N'-bis(4'-aminophenyl)-1,3-diaminopropanol." However, this should recite "N,N'-bis(ß-hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol." The mistake is the space between "-N," and "N'." This space, coming after a comma within the formula, may lead to confusion. Specifically, it is not clear, as published, whether the above discloses one or two compounds. Thus, this mistake is material as it may affect the public's ability to appreciate the technical disclosure of the patent application publication. For at least this reason, this mistake is material and accordingly should be corrected.
- 7. In line 2 of paragraph 111, the published application recites "NR<sub>18</sub>RL<sub>19</sub>." However, this should recite "NR<sub>18</sub>R<sub>19</sub>." This mistake, therefore, results in the disclosure of an erroneous formula. Thus, this mistake is material as it may affect the public's ability to appreciate the technical disclosure of the patent application publication. For at least this reason, this mistake is material

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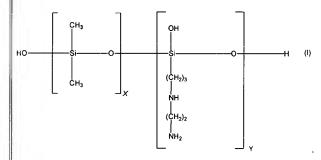
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and accordingly should be corrected.

8. In claim 8, the published application recites as formula (I)



However, the originally filed application recites as formula (I):



The error is that the published application recites "CH<sub>32</sub>" rather than " CH<sub>3</sub>." This mistake, therefore, results in the disclosure of an erroneous formula. Thus, this mistake is material as it may affect the public's ability to appreciate the technical disclosure of the patent application publication. For at least this reason, this mistake is material and accordingly should be corrected.

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9. In claim 8, the published application recites as formula (II)

$$R_aG_{3 \rightarrow a}\text{-}Si \ (OSiG_2)_n\text{-}(OSiG_bR_{2\text{-}b})_{m\text{-}O\text{-}SiG3\text{-}a\text{-}Ra}$$
  $R_a$ 

However, this formula should recite:  $R_aG_{3-a}$ -Si(OSi $G_2$ )<sub>n</sub>-(OSi $G_bR_{2-b}$ )<sub>m</sub>-O-Si $G_{3-a}$ -R<sub>a</sub>. This mistake, therefore, results in the disclosure of an erroneous formula. Thus, this mistake is material as it may affect the public's ability to appreciate the technical disclosure of the patent application publication. For at least this reason, this mistake is material and accordingly should be corrected.

10. In claim 8, in the definition of R, the published application recites:

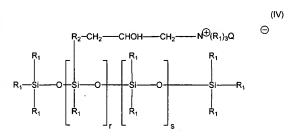
whereas, it should recite:

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These mistakes are material as they may affect the public's ability to appreciate the technical disclosure of the patent application publication. For at least this reason, these mistakes are material and accordingly should be corrected.

11. In claim 8, the published application, the formula (IV) recites:



whereas, it should recite:

$$R_{2}-CH_{2}-CHOH-CH_{2}-N^{\bigoplus}(R_{1})_{3}Q^{\bigodot}$$

$$R_{1}-S_{1}-O -S_{1}-O -S_{1}-O -S_{1}-O -S_{1}-O -S_{1}-R_{1}$$

The error is that the sign " " is not beside the Q group, and thus does not accurately represent that the Q group is a negatively charged ion, and may be erroneously interpreted as representing that the entire cationic silicone polymer of formula (IV) is negatively charged. This mistake is material as it may affect the public's ability to appreciate the technical disclosure of the patent application

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publication. For at least this reason, this mistake is material and accordingly should be corrected.

For at least the foregoing reasons, Applicants request that the Office correct the mistakes identified above for which the Office is at fault in the published application, and forward to Applicants a copy of the corrected published application or at least a notification of the occurrence or predicted occurrence of the corrected publication once it has been corrected.

Applicants believe that no Petition or fee is due in connection with this Request. However, if any Petition or fee is due, please grant the Petition and charge the fee to our Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,

GARRETT & DUNNER, L.L.P.

Thalia V. Warnement Registration No. 39,064

Date: February 8, 2002

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as regards the compatibility of permanent-waved or bleached hair with subsequent treatments, as regards the degradation of the mechanical properties of the permanentwaved hair, in particular the reduction of the porosity of the hair, and as regards the reduction of the cosmetic properties such as the feel, or alternatively as regards the uniformity of the bleaching along the keratin fibres.

[0015] The aim of the present invention is to solve the problems mentioned above.

[0016] The Applicant has discovered, surprisingly, novel compositions containing, as oxidizing system, at least one enzyme of 2-electron oxidoreductase type in the presence of at least one donor for the said enzyme and at least one aminosilicone, which can constitute, in the presence of oxidation dye precursors (oxidation bases) and optionally couplers, ready-to-use dye formulations which lead to more homogeneous, more intense and more chromatic colorations without giving rise to any significant degradation, these colorations being relatively unselective and showing good resistance to the various aggressive factors to which the hair may be subjected.

[0017] The Applicant has also discovered, unexpectedly, that the use, in a process for the permanent reshaping of keratin fibres, of an oxidizing composition containing, as oxidizing system, at least one enzyme of 2-electron oxidoreductase type in the presence of at least one donor for the said enzyme and at least one aminosilicone, makes it possible to solve the technical problems mentioned above. In particular, this type of oxidizing composition improves the curl hold obtained over time, substantially reduces the porosity of permanent-waved hair and improves the compatibility of permanent-waved hair with respect to subsequent treatments.

[0018] The Applicant has also discovered, surprisingly, that the use, in a process for bleaching keratin fibres, of an oxidizing composition containing, as oxidizing system, at least one enzyme of 2-electron oxidoreductase type in the presence of at least one donor for the said enzyme and at least one aminosilicone, makes it possible to solve the technical problems mentioned above, in particular to improve the compatibility of bleached hair with respect to subsequent treatments. This type of oxidizing composition gives a more uniform bleaching effect on the hair and improves the cosmetic properties, such as the feel.

[0019] These discoveries form the basis of the present invention.

[0020] The subject of the present invention is thus, firstly, a cosmetic and/or dermatological composition intended for treating keratin fibres, in particular human keratin fibres and more particularly human hair, comprising, in a support which is suitable for keratin fibres:

[0021] (a) at least one enzyme of 2-electron oxidoreductase type in the presence of at least one donor for the said enzyme,

[0022] (b) at least one aminosilicone.

[0023] The 2-electron oxidoreductase(s) used in the oxidizing compositions in accordance with the invention can be chosen in particular from pyranose oxidases, glucose oxidases, glycerol oxidases, lactate oxidases, pyruvate oxidases and uricases.

[0024] According to the invention, the 2-electron oxidoreductase is preferably chosen from uricases of animal, microbiological or biotechnological origin.

[0025] By way of example, mention may be made in particular of uricase extracted from boar liver, uricase from Astrhrobacter globiformis, as well as uricase from Aspergillus flavus.

[0026] The 2-electron oxidoreductase(s) can be used in pure crystalline form or in a form diluted in a dilutent which is inert with respect to the said 2-electron oxidoreductase.

[0027] The 2-electron oxidoreductase(s) in accordance with the invention preferably represent(s) from 0.01 to 20% by weight approximately relative to the total weight of the composition, and even more preferably from 0.1 to 5% by weight approximately relative to this weight.

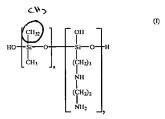
[0028] According to the invention, the term donor is understood to refer to the various substrates also necessary for the functioning of the said 2-electron oxidoreductase(s).

[0029] The nature of the donor (or substrate) for the said enzyme varies depending on the nature of the 2-electron oxidoreductase used. For example, as donors for the pyranose oxidases, mention may be made of D-glucose, L-sorbose and D-xylose; as a donor for the glucose oxidases, mention may be made of D-glucose; as donors for the glycerol oxidases, mention may be made of glycerol and dihydroxyacetone; as donors for the lactate oxidases, mention may be made of lactic acid and its salts; as donors for the pyruvate oxidases, mention may be made of pyruvic acid and its salts; and lastly, as donors for the uricases, mention may be made of uric acid and its salts.

[0030] The donor(s) (or substrate(s)) used in accordance with the invention preferably represent(s) from 0.01 to 20% by weight approximately relative to the total weight of the composition in accordance with the invention, and even more preferably from 0.1 to 5% approximately relative to this weight.

[0031] According to the invention, the term aminosilicone is understood to denote any silicone containing at least one primary, secondary or tertiary amine or a quaternary ammonium group. Mention may thus be made of:

[0032] (a) the polysiloxanes referred to in the CTFA dictionary as "amodimethicone" and corresponding to formula (I):



[0033] in which x and y are integers dependent on the molecular weight, generally such that the said number-average molecular weight is between 5000 and 500,000 approximately;

[0034] (b) cationic silicone polymers corresponding to the formula:

$$R_{\bullet}G_{3-\bullet}-Si(OSiG_{2})_{\mathfrak{n}}-(OSiG_{\mathfrak{b}}R_{2-\mathfrak{b}})_{\mathfrak{m}}-O-SiG_{3-\bullet}-R_{\bullet}(\mathfrak{I}\mathfrak{l})$$

[0035] in which:

[0036] G is a hydrogen atom or a phenyl, OH or C<sub>1</sub>-C<sub>8</sub> alkyl, for example methyl, group,

[0037] a denotes the number 0 or an integer from 1 to 3, in particular 0,

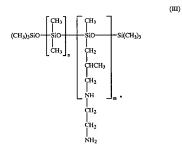
[0038] b denotes 0 or 1, and in particular 1,

[0039] m and n are numbers such that the sum (n+m) can range especially from 1 to 2000 and in particular from 50 to 150, it being possible for n to denote a number from 0 to 1999 and in particular from 49 to 149, and it being possible for m to denote a number from 1 to 2000 and in particular from 1 to 10;

[0040] R is a monovalent radical of formula — $C_qH_{2q}L$  in which q is a number from 2 to 8 and L is an optionally quaternized amine group chosen from the groups:

[0047] in which R'can denote hydrogen, phenyl, benzyl or a monovalent, saturated hydrocarbon-based radical, for example an alkyl radical containing from 1 to 20 carbon atoms, and A" represents a halide ion such as, for example, fluoride, chloride, bromide or iodide.

[0048] A product corresponding to this definition is the polymer known as "trimethylsilylamodimethicone" corresponding to formula (III) below:



[0049] in which n and m have the meanings given above for formula (II). Such polymers are described, for example, in patent application EP-A-95238.

[0050] (c) cationic silicone polymers corresponding to the formula:

$$\begin{array}{c} R_{2}-CH_{2}-CHOH-CH_{2}-N^{\oplus}(R_{1})Q \\ \hline \\ R_{1}-S_{1}-O-S_{$$

[0051] in which

[0052]  $R_1$  represents a monovalent hydrocarbon-based radical containing from 1 to 18 carbon atoms, and in particular a  $C_1$ - $C_{18}$ , alkyl radical or a  $C_2$ - $C_{18}$  alkenyl radical, for example methyl:

[0053] R<sub>2</sub> represents a divalent hydrocarbon-based radical, in particular a C<sub>1</sub>-C<sub>18</sub> alkylene radical or a C<sub>1</sub>-C<sub>18</sub>, for example C<sub>1</sub>-C<sub>8</sub>, divalent alkylenoxy radical;

[0054] Q is a halide ion, in particular chloride;

[0055] r represents an average statistical value from 2 to 20 and in particular from 2 to 8;

[0056] s represents an average statistical value from 20 to 200 and in particular from 20 to 50.

[0057] Such polymers are described more particularly in U.S. Pat. No. 4,185,087.

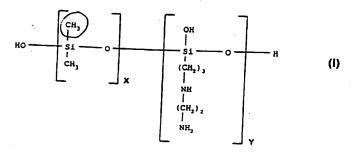
[0058] One polymer belonging to this class is the polymer sold by the company Union Carbide under the name "Ucar Silicone ALE 56".

[0059] When these silicone polymers are used, one particularly advantageous embodiment is their use together with cationic and/or nonionic surfactants.

[0060] It is possible, for example, to use the product sold under the name "Cationic Emulsion DC 929" by the company Dow Corning, which comprises, besides amodimethicone, a cationic surfactant comprising a mixture of products corresponding to the formula:

[0061] in which R<sub>3</sub> denotes alkenyl and/or alkyl radicals containing from 14 to 22 carbon atoms, derived from tallow fatty acids, and known under the CTFA name "tallowtrimonium chloride", in combination with a nonionic surfactant of formula: C<sub>9</sub>H<sub>1.9</sub>—C<sub>9</sub>H<sub>4</sub>—(OC<sub>2</sub>H<sub>4</sub>)<sub>10</sub>—OH, known under the name "Nonoxynol 10".

[0062] Use may also be made, for example, of the product sold under the name "Cationic Emulsion DC 939" by the company Dow Corning, which comprises, besides amodimethicone, a cationic surfactant which is trimethylectylammonium chloride, in combination with a nonionic surfactant of formula  $C_{13}H_{27}$ — $(OC_2H_4)_2$ —OH, known under the CTFA name "trideceth-12".



in which x and y are integers dependent on the molecular weight, generally such that the said number-average molecular weight is between 5000 and 500,000 approximately;

(b) cationic silicone polymers corresponding to the formula:

$$R_aG_{3-a}-Si(OSiG_2)_n-(OSiG_bR_{2-b})_m-O-SiG_{3-a}-R_a$$
 (II)

10 in which:

G is a hydrogen atom or a phenyl, OH or  $C_1\text{--}C_8$  alkyl, for example methyl, group,

a denotes the number 0 or an integer from 1 to 3, in particular 0,

b denotes 0 or 1, and in particular 1, m and n are numbers such that the sum (n + m) can range especially from 1 to 2000 and in particular from 50 to 150, it being possible for n to denote a number from 0 to 1999 and in particular from 49 to 149, and it being possible for m to denote a number from 1 to 2000 and in

R is a monovalent radical of formula  $-C_qH_{2q}L$  in which q is a number from 2 to 8 and L is an optionally quaternized amine group chosen from the groups:

25  $-N(R')-CH_2-CH_2-N(R')_2$ 

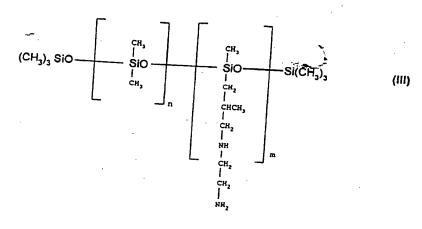
particular from 1 to 10;

$$-N (R')_{2}$$
 $-N^{\oplus} (R')_{3}A^{-}$ 
 $-N^{\oplus} (R')_{2} (H) A^{-}$ 

 $-N^{\oplus}(R') (H)_{2}A^{-}$   $-N (R') -CH_{2}-CH_{2}-N^{\oplus}(R') (H)_{2}A^{-}$ 

in which R' can denote hydrogen, phenyl, benzyl or a monovalent, saturated hydrocarbon-based radical, for example an alkyl radical containing from 1 to 20 carbon atoms, and A represents a halide ion such as, for example, fluoride, chloride, bromide or iodide.

A product corresponding to this definition is the polymer known as "trimethylsilylamodimethicone" 10 corresponding to formula (III) below:



in which n and m have the meanings given above for formula (II). Such polymers are described, for example, in patent application EP-A-95238.

(c) cationic silicone polymers corresponding to the formula:

$$R_{1} = \begin{bmatrix} R_{2} - CH_{2} - CHOH - CH_{2} - N & (R_{1})_{3} & Q \\ R_{1} - SI - O + SI - O + SI - O + SI - R_{1} \\ R_{1} - R_{1} \end{bmatrix} \begin{bmatrix} R_{1} & R_{1} \\ R_{1} & R_{1} \end{bmatrix}$$

$$(IV)$$

[0063] Another commercial product which can be used according to the invention is the product sold under the name "Dow Corning Q2 7224" by the company Dow Corning, containing, in combination, trimethyl-silylamodimethicone of formula (III) described above, a nonionic surfactant of formula: Cf12-7-C<sub>6</sub>H<sub>4</sub>-(OCH<sub>2</sub>CH<sub>2</sub>)<sub>40</sub>-OH, known under the CTKA-name "octoxynol-40", a second nonionic surfactant of formula: C<sub>12</sub>H<sub>25</sub>-(OCH<sub>2</sub>-CH<sub>2</sub>)<sub>6</sub>-OH, known under the CTFA name "isolaureth-6", and propylene abyeral

[0064] The compositions in accordance with the invention contain the aminosilicones defined above at weight contents which can be between 0.05% and 10%, preferably between 0.1% and 5% and even more preferably between 0.2% and 3%, relative to the total weight of the composition.

[0065] A subject of the present invention is also a readyto-use composition for the oxidation dyeing of keratin fibres, and in particular human keratin fibres such as the hair, of the type comprising, in a medium which is suitable for dyeing, at least one oxidation base and, where appropriate, one or more couplers, which is characterized in that it contains:

[0066] (a) at least one enzyme of 2-electron oxidoreductase type in the presence of at least one donor for the said enzyme,

[0067] (b) at least one aminosilicone.

[0068] The nature of the oxidation base(s) used in the ready-to-use dye composition is not a critical factor. They can be chosen, in particular, from para-phenylenediamines, double bases, para-aminophenols, ortho-aminophenols and heterocyclic oxidation bases.

[0069] Among the para-phenylenediamines which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made in particular of the compounds of formula (V) below, and the addition salts thereof with an acid:

$$R_7$$
 $R_7$ 
 $R_6$ 
 $R_7$ 
 $R_8$ 

[0070] in which:

[0071] R<sub>4</sub> represents a hydrogen atom, a C<sub>1</sub>-C<sub>4</sub> alkyl radical, a C<sub>2</sub>-C<sub>4</sub> monohydroxyalkyl radical, a C<sub>2</sub>-C<sub>4</sub> polyhydroxyalkyl radical, a (C<sub>1</sub>-C<sub>4</sub>)alkoxy(C<sub>1</sub>-C<sub>4</sub>)alkyl radical, a C<sub>1</sub>-C<sub>4</sub> alkyl radical substituted with a nitrogenous group, a phenyl radical or a 4-aminophenyl radical;

[0072] R<sub>3</sub> represents a hydrogen atom, a C<sub>1</sub>-C<sub>4</sub> alkyl radical, a C<sub>1</sub>-C<sub>4</sub> monohydroxyalkyl radical, a C<sub>2</sub>-C<sub>4</sub> polyhydroxyalkyl radical, a (C<sub>1</sub>-C<sub>4</sub>)alkoxy(C<sub>1</sub>-C<sub>4</sub>)alkyl radical or a C<sub>1</sub>-C<sub>4</sub> alkyl radical substituted with a nitrogenous group;

[0073] R<sub>6</sub> represents a hydrogen atom, a halogen atom such as a chlorine, bromine, iodine or fluorine atom, a C<sub>1</sub>-C<sub>4</sub> alkyl radical, a C<sub>1</sub>-C<sub>4</sub> monohydroxyalkyl radical, a C<sub>1</sub>-C<sub>4</sub> hydroxyalkoxy radical, a cylamino (C<sub>1</sub>-C<sub>4</sub>) alkoxy radical, a C<sub>1</sub>-C<sub>4</sub> mesylaminoalkoxy radical or a carbamoylamino(C<sub>1</sub>-C<sub>4</sub>)alkoxy radical.

[0074] R<sub>7</sub> represents a hydrogen or halogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl radical.

[0075] Among the nitrogenous groups of formula (V) above, mention may be made in particular of amino, mono(C<sub>1</sub>-C<sub>4</sub>)alkylamino, di(C<sub>1</sub>-C<sub>4</sub>)alkylamino, tri (C<sub>1</sub>-C<sub>4</sub>)alkylamino, monohydroxy(C<sub>1</sub>-C<sub>4</sub>)alkylamino, imidazolinium and ammonium radicals.

[0076] Among the para-phenylenediamines of formula (V) above, mention may be made more particularly of para-phenylenediamine, para-toluylenediamine, 2-chloro-2,3-dimethyl-para-phenylenedipara-phenylenediamine, amine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethylpara-phenylenediamine, 2,5-dimethyl-paraphenylenediamine, N,N-dimethyl-para-phenylenediamine, N,N-diethyl-para-phenylenediamine, N,N-dipropyl-paraphenylenediamine, 4-amino-N,N-diethyl-3-methylaniline, N,N-bis(β-hydroxyethyl)-para-phenylenediamine, 4-amino-N,N-bis(β-hydroxyethyl)-2-methylaniline, 4-amino-2chloro-N,N-bis(β-hydroxyethyl)aniline, 2-β-hydroxyethylpara-phenylenediamine, 2-fluoro-para-phenylenediamine, 2-isopropyl-para-phenylenediamine, N-(\beta-hydroxypropyl)para-phenylenediamine, 2-hydroxymethyl-para-phenylenediamine, N,N-dimethyl-3-methyl-para-phenylenediamine, N,N-(ethyl-β-hydroxyethyl)-para-phenylenediamine, N-(β, γ-dihydroxypropyl)-para-phenylene-diamine, N-(4'-aminophenyl)-para-phenylenediamine, N-phenyl-para-phenylenediamine, 2-β-hydroxyethyloxy-paraphenylenediamine, 2-\u03b3-acetylaminoethyloxy-paraphenylenediamine and N-(β-methoxyethyl)-paraphenylenediamine, and the addition salts thereof with an

[0077] Among the para-phenylenediamines of formula (V) above, para-phenylenediamine, para-toluylenediamine, 2-β-hydroxyethyl-para-phenylenediamine, 2-β-hydroxyethyl-para-phenylenediamine, 2-β-hydroxyethyloxy-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, 2,6-hydroxyethyl)-para-phenylenediamine, 2-chloro-para-phenylenediamine and 2-β-acetylaminoethyloxy-para-phenylenediamine and the addition salts thereof with an acid are most particularly preferred.

[0078] According to the invention, the term double bases is understood to refer to the compounds containing at least two aromatic rings bearing amino and/or hydroxyl groups.

[0079] Among the double bases which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made in particular of the compounds corresponding to formula (VI) below, and the addition salts thereof with an acid:

nonionic surfactant of formula:  $C_9H_{19}-C_6H_4-(OC_2H_4)_{10}-OH$ , known under the name "Nonoxynol 10".

Use may also be made, for example, of the product sold under the name "Cationic Emulsion DC 939" by the company Dow Corning, which comprises, besides amodimethicone, a cationic surfactant which is trimethylcetylammonium chloride, in combination with a nonionic surfactant of formula C<sub>13</sub>H<sub>27</sub>-(OC<sub>2</sub>H<sub>4</sub>)<sub>12</sub>-OH, known under the CTFA name "trideceth-12".

- Another commercial product which can be used according to the invention is the product sold under the name "Dow Corning Q2 7224" by the company Dow Corning, containing, in combination, trimethylsilylamodimethicone of formula (III) described above, a nonionic surfactant of formula: C<sub>9</sub>H<sub>17</sub>-C<sub>6</sub>H<sub>4</sub>-(OCH<sub>2</sub>CH<sub>2</sub>)<sub>40</sub>-OH,
- nonionic surfactant of formula:  $(C_8H_{17}-C_6H_4-(OCH_2CH_2)_{40}-OH$ , known under the CTFA name "octoxynol-40", a second nonionic surfactant of formula:  $C_{12}H_{25}-(OCH_2-CH_2)_6-OH$ , known under the CTFA name "isolaureth-6", and propylene glycol.
- The compositions in accordance with the invention contain the aminosilicones defined above at weight contents which can be between 0.05% and 10%, preferably between 0.1% and 5% and even more preferably between 0.2% and 3%, relative to the total weight of the composition.

A subject of the present invention is also a ready-to-use composition for the oxidation dyeing of keratin fibres, and in particular human keratin fibres such as the hair, of the type comprising, in a medium which is suitable for dyeing, at least one oxidation base and, where appropriate, one or more couplers, which is characterized in that it contains:

- (a) at least one enzyme of 2-electron oxidoreductase type in the presence of at least one donor for the said35 enzyme,
  - (b) at least one aminosilicone.

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 $\begin{bmatrix} Z_1 & & & & \\ & Z_2 & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & &$ 

[0080] in which:

[0081] Z<sub>1</sub>, and Z<sub>2</sub>, which may be identical or different, represent a hydroxyl or —NH<sub>2</sub> radical which may be substituted with a C<sub>1</sub>-C<sub>1</sub> (1) lkyl radical or with a linker arm Y;

[0082] the linker arm Y represents a linear or branched alkylene chain containing from 1 to 15 carbon atoms, which may be interrupted by or terminated with one or more nitrogenous groups and/or one or more hetero atoms such as oxygen, sulphur or nitrogen atoms, and optionally substituted with one or more hydroxyl or C<sub>1</sub>-C<sub>6</sub> alkoxy radicals;

[0083] R<sub>a</sub> and R<sub>2</sub>, represent a hydrogen or halogen atom, a C<sub>1</sub>-C<sub>4</sub> alkyl radical, a C<sub>1</sub>-C<sub>4</sub> monohydroxyalkyl radical, a C<sub>2</sub>-C<sub>4</sub> polyhydroxyalkyl radical, a C<sub>1</sub>-C<sub>4</sub> aminoalkyl radical or a linker arm Y;

[0084] R<sub>10</sub>, R<sub>11</sub>, R<sub>12</sub>, R<sub>13</sub>, R<sub>14</sub> and R<sub>15</sub>, which may be identical or different, represent a hydrogen atom, a linker arm Y or a C<sub>1</sub>-C<sub>4</sub> alkyl radical;

[0085] it being understood that the compounds of formula (VI) contain only one linker arm Y per molecule.

[0086] Among the nitrogenous groups of formula (VI) above, mention may be made in particular of amino, mono(C<sub>1</sub>-C<sub>4</sub>)alkylamino, di(C<sub>1</sub>-C<sub>4</sub>)alkylamino, tri(C<sub>1</sub>-C<sub>4</sub>)alkylamino, monohydroxy(C<sub>1</sub>-C<sub>4</sub>)alkylamino, imidazolinium and ammonium radicals.

[0087] Among the double bases of formula (VI) above, mention may be made more particularly of N,N'-bis(β-hydroxyethyl)-N, N'-bis(4'-aminophenyl)-1,3-diaminopropanol, N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)-tetramethylenediamine, N,N'-bis(6'-aminophenyl)-tetramethylenediamine, N,N'-bis(6'-aminophenyl)-tetramethylaminophenyl)\tetramethylenediamine, N,N'-bis(4'-aminophenyl)\tetramethylenediamine, N,N'-bis(4'-amino-3'-methylphenyl)\tetramethylenediamine and 1,8-bis(2,5-methylphenyl)\tetramethylenediamine

methylphenyl)ethylenediamine and 1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane, and the addition salts thereof with an acid.

[0088] Among these double bases of formula (VI), N,N-bis(β-hydroxyethyl)-N,N-bis(4'-aminophenopyl)-1,3-di-aminopropanol and 1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane, or one of the addition salts thereof with an acid, are particularly preferred.

[0089] Among the para-aminophenols which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made in particular of the

compounds corresponding to formula (VII) below, and the addition salts thereof with an acid:

(VII) OH  $R_{16}$   $R_{17}$ 

[0090] in which:

[0091] R<sub>1.6</sub> represents a hydrogen or halogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> monohydroxyalkyl, C<sub>1</sub>-C<sub>4</sub> C<sub>4</sub>)alkoxy(C<sub>1</sub>-C<sub>4</sub>)alkyl, C<sub>1</sub>-C<sub>4</sub> aminoalkyl C<sub>1</sub> or hydroxy(C<sub>1</sub>-C<sub>4</sub>)alkylamino-(C<sub>1</sub>-C<sub>4</sub>)alkyl radical,

[0092] R<sub>17</sub> represents a hydrogen or halogen atom or a C<sub>1</sub>-C<sub>4</sub>-alkyl, C<sub>2</sub>-C<sub>4</sub> monohydroxyalkyl, C<sub>2</sub>-C<sub>4</sub> polyhydroxyalkyl, C<sub>1</sub>-C<sub>4</sub> aminoalkyl, C<sub>1</sub>-C<sub>4</sub> cyanoalkyl or (C<sub>1</sub>-C<sub>4</sub>)alkoxy-(C<sub>1</sub>-C<sub>4</sub>)alkyl radical,

[0093] it being understood that at least one of the radicals  $R_{16}$  or  $R_{17}$  represents a hydrogen atom.

[0094] Among the para-aminophenols of formula (VII) above, mention may be made more particularly of para-aminophenol, 4-amino-3-fluorophenol, 4-amino-3-fluorophenol, 4-amino-3-hydroxymethylphenol, 4-amino-2-methylphenol, 4-amino-2-hydroxymethylphenol, 4-amino-2-methoxymethylphenol, 4-amino-2-aminomethylphenol, 4-amino-2-fluorophenol, and the addition salts thereof with an acid.

[0095] Among the ortho-aminophenols which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made more particularly of 2-aminophenol, 2-amino-5-methylphenol and 5-acetamido-2-aminophenol, and the addition salts thereof with an acid.

[0096] Among the heterocyclic bases which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made more particularly of pyridine derivatives, pyrimidine derivatives, pyrazole derivatives and pyrazolopyrimidine derivatives, and the addition salts thereof with an acid.

[0097] Among the pyridine derivatives, mention may be made more particularly of the compounds described, for example, in patents GB 1,026,978 and GB 1,153,196, such as 2,5-diaminopyridine, 2-(4-methoxyphenyl)amino-3-aminopyridine, 2,3-diamino-6-methoxypyridine, 2-(β-methoxyethyl)amino-3-amino-6-methoxypyridine and 3,4-diaminopyridine, and the addition salts thereof with an acid.

[0098] Among the pyrimidine derivatives, mention may be made more particularly of the compounds described, for example, in German patent DE 2,359,399 or Japanese patent JP 88-169,571 or patent application WO 96/15765, such as 2,4,5,6-tetraaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 2,4-dihy-

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phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,3-dimethyl-paraphenylenediamine,  $N, N-bis(\beta-hydroxyethyl)-para$ phenylenediamine, 2-chloro-para-phenylenediamine and 2- $\beta$ -acetylaminoethyloxy-para-phenylenediamine and the addition salts thereof with an acid are most particularly preferred.

According to the invention, the term double bases is understood to refer to the compounds containing at least two aromatic rings bearing amino and/or hydroxyl groups.

Among the double bases which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made in particular of the compounds corresponding to formula (VI) below, and the addition salts thereof with an acid:

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in which:

- $Z_1$  and  $Z_2$ , which may be identical or different, represent a hydroxyl or -NH $_2$  radical which may be substituted with a  $C_1$ - $C_4$  alkyl radical or with a linker arm Y;
- the linker arm Y represents a linear or branched alkylene chain containing from 1 to 14 carbon atoms, which may be interrupted by or terminated with one or more nitrogenous groups and/or one or more hetero atoms such as oxygen, sulphur or nitrogen atoms, and

optionally substituted with one or more hydroxyl or C<sub>1</sub>-C<sub>6</sub> alkoxy radicals;

- $R_8$  and  $R_9$  represent a hydrogen or halogen atom, a  $C_1-C_4$  alkyl radical, a  $C_1-C_4$  monohydroxyalkyl radical, a  $C_2-C_4$  polyhydroxyalkyl radical, a  $C_1-C_4$ aminoalkyl radical or a linker arm Y;
- $R_{10},\ R_{11},\ R_{12},\ R_{13},\ R_{14}$  and  $R_{15},$  which may be identical or different, represent a hydrogen atom, a linker arm Y or a  $C_1-C_4$  alkyl radical;
- it being understood that the compounds of formula (VI) contain only one linker arm Y per molecule.

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Among the nitrogenous groups of formula (VI) above, mention may be made in particular of amino, mono( $C_1-C_4$ ) alkylamino, di( $C_1-C_4$ ) alkylamino, tri(C1- $C_4$ ) alkylamino, monohydroxy  $(C_1-C_4)$  alkylamino, linium and ammonium radicals.

Among the double bases of formula (VI) above, mention may be made more particularly of N,N'-bis $(\beta$ hydroxyethyl) (N,N)'-bis(4'-aminophenyl)-1,3-diaminopro-N,N'-bis( $\beta$ -hydroxyethyl)-N,N'-bis(4'-aminophenyl) ethylenediamine, N, N'-bis(4-aminophenyl)tetramethylenediamine, N,N'-bis $(\beta$ -hydroxyethyl)-N,N'bis(4-aminophenyl)tetramethylenediamine, N, N'-bis (4methylaminophenyl) tetramethylenediamine,

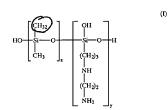
N, N'-bis-

(ethyl)-N,N'-bis(4'-amino-3'-methylphenyl)ethylenedi-25 amine and 1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane, and the addition salts thereof with an acid.

Among these double bases of formula (VI), N,N'bis( $\beta$ -hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol 1,8-bis(2,5-diaminophenoxy)-3,5and dioxaoctane, or one of the addition salts thereof with an acid, are particularly preferred.

Among the para-aminophenols which can be used oxidation bases in the dye compositions accordance with the invention, mention may be made in 35 particular of the compounds corresponding to formula

- 8. Composition according to any one of claims 1 to 7, characterized in that the aminosilicone is chosen from:
  - (a) the polysiloxanes corresponding to the formula:

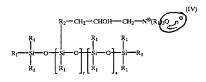


- in which x and y are integers dependent on the molecular weight, generally such that the said number-average molecular weight is between 5000 and 500,000 approximately;
- (b) cationic silicone polymers corresponding to the for-

- G is a hydrogen atom or a phenyl, OH or C<sub>1</sub>-C<sub>8</sub> alkyl, for example methyl, group,
- a denotes the number 0 or an integer from 1 to 3, in particular 0,
- b denotes 0 or 1, and in particular 1,
- m and n are numbers such that the sum (n+m) can range especially from 1 to 2000 and in particular from 50 to 150, it being possible for n to denote a number from 0 to 1999 and in particular from 49 to 149, and it being possible for m to denote a number from 1 to 2000 and in particular from 1 to 10;
- R is a monovalent radical of formula C<sub>q</sub>H<sub>2q</sub>L in which q is a number from 2 to 8 and L is an optionally quaternized amine group chosen from the groups:

$$\begin{array}{l} -N(R') - CH_2 - CH_2 - N(R)_2 \\ -N(R')_2 \\ -N^{\mathbb{Q}(R')_3 A} - \\ -N^{\mathbb{Q}(R')_2(H)A} - \\ -N^{\mathbb{Q}(R')(H)2A} - \\ -N(R') - CH_2 - CH_2 - N^{\mathbb{Q}(R')(H)2A}; \end{array}$$

- in which R' can denote hydrogen, phenyl, benzyl or a monovalent, saturated hydrocarhon-based radical, for example an alkyl radical containing from 1 to 20 carbon atoms, and A represents a halide ion such as, for example, fluoride, chloride, bromide or iodide.
- (c) cationic silicone polymers corresponding to the formula:



in which

- R<sub>1</sub> represents a monovalent hydrocarbon-based radical containing from 1 to 18 carbon atoms, and in particular a C<sub>1</sub>-C<sub>18</sub> alkyl radical or a C<sub>2</sub>-C<sub>18</sub> alkenyl radical, for example methyl;
- R<sub>2</sub> represents a divalent hydrocarbon-based radical, in particular a C<sub>1</sub>-C<sub>18</sub> alkylene radical or a C<sub>1</sub>-C<sub>18</sub>, for example C<sub>1</sub>-C<sub>8</sub>, divalent alkylenoxy radical;
- Q<sup>-</sup> is a halide ion, in particular chloride; r represents an average statistical value from 2 to 20 and in particular from 2 to 8;
- s represents an average statistical value from 20 to 200 and in particular from 20 to 50.
- 9. Composition according to any one of claims 1 to 8, characterized in that the concentration of aminosilicone ranges from 0.05% to 10% by weight relative to the total weight of the composition, and preferably between 0.1 and 56.
- 10. Ready-to-use composition according to any one of claims 1 to 9, for the oxidation dyeing of keratin fibres, and in particular human keratin fibres such as the hair, of the type also comprising, in a medium which is suitable for keratin fibres, at least one oxidation base and, optionally, one or more couplers.
- 11. Composition according to claim 10, characterized in that the oxidation bases are chosen from para-phenylenediamines, double bases, ortho- or para-aminophenols and heterocyclic bases, as well as the addition salts of these compounds with an acid.
- 12. Composition according to claim 10 or 11, characterized in that the oxidation bases are present in concentrations ranging from 0.0005 to 12% by weight relative to the total weight of the composition.
- 13. Composition according to claim 10, characterized in that the couplers are chosen from meta-phenylenediamines, meta-aminophenols, meta-diphenols and heterocyclic couplers, and the addition salts of these compounds with an acid.
- 14. Composition according to claim 10 or 13, characterized in that the couplers are present in concentrations ranging from 0.0001 to 10% by weight relative to the total weight of the composition.
- 15. Composition according to claim 11 or 13, characterized in that the addition salts with an acid for the oxidation bases and the couplers are chosen from the hydrochlorides, hydrobromides, sulphates, tartrates, lactates and acctates.
- 16. Composition according to any one of claims 10 to 15, characterized in that it also contains direct dyes.
- 17. Composition according to any one of claims 1 to 16, characterized in that the medium which is suitable for the

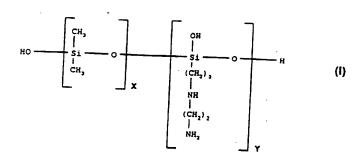
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from:

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(a) the polysiloxanes corresponding to the formula:



in which x and y are integers dependent on the molecular weight, generally such that the said number-average molecular weight is between 5000 and 500,000 approximately;

(b) cationic silicone polymers corresponding to the formula:

$$R_aG_{3-a}-Si(OSiG_2)_n-(OSiG_bR_{2-b})_m-O-SiG_{3-a}-R_a$$
 (II) in which:

G is a hydrogen atom or a phenyl, OH or  $C_1\text{--}C_8$  alkyl, for example methyl, group,

a denotes the number  ${\tt 0}$  or an integer from 1 to 3, in particular  ${\tt 0}$ ,

b denotes 0 or 1, and in particular 1,

20 m and n are numbers such that the sum (n + m) can range especially from 1 to 2000 and in particular from 50 to 150, it being possible for n to denote a number from 0 to 1999 and in particular from 49 to 149, and it being possible for m to denote a number from 1 to 2000 and in particular from 1 to 10:

R is a monovalent radical of formula  $-C_qH_{2q}L$  in which q is a number from 2 to 8 and L is an optionally quaternized amine group chosen from the groups:

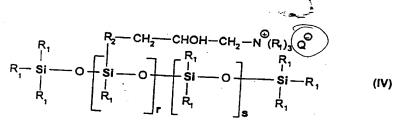
$$-N(R')$$
 -  $CH_2$  -  $CH_2$  -  $N(R')_2$   
 $-N(R')_2$   
 $-N(R')_3$   
 $-N(R')_2(H)A$ 

5 -N (R') (H) 2A

-N(R')-CH<sub>2</sub>-CH<sub>2</sub>-N<sup>®</sup>(R')(H)<sub>2</sub>A<sup>-</sup>;

in which R' can denote hydrogen, phenyl, benzyl or a monovalent, saturated hydrocarbon-based radical, for example an alkyl radical containing from 1 to 20 carbon atoms, and A represents a halide ion such as, for example, fluoride, chloride, bromide or iodide.

(c) cationic silicone polymers corresponding to the formula:



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in which

 $R_1$  represents a monovalent hydrocarbon-based radical containing from 1 to 18 carbon atoms, and in particular 20 a  $C_1$ - $C_{18}$  alkyl radical or a  $C_2$ - $C_{18}$  alkenyl radical, for example methyl;

 $R_2$  represents a divalent hydrocarbon-based radical, in particular a  $C_1-C_{18}$  alkylene radical or a  $C_1-C_{18}$ , for example  $C_1-C_8$ , divalent alkylenoxy radical;

- 25 Q is a halide ion, in particular chloride;
   r represents an average statistical value from 2 to 20
   and in particular from 2 to 8;
  - s represents an average statistical value from 20 to  $200\,$  and in particular from  $20\,$  to  $50\,$ .
- 30 9. Composition according to any one of Claims 1 to